OST Technical Progress Report
Clean Water Team--FY 2001 Results

Team Members: Terry E. Ackman (Team Leader), Lyn Brickett, Ethel Burse, Bob Dilmore (Univ. of Pittsburgh), Hank Edenborn, Fouzan AL-Fouzan (University of Pittsburgh), Larry Gioia, (Gannon College), Don Harrison, Rick Hammack, Pete Hesbach, Candace Kairies (Univ. of Pittsburgh), Andy Kociban, Steve Lamey, Jim Sams (USGS), Karl Schroeder, Jennifer Shogren (West Virginia University), Garret Veloski, and George Watzlaf.

Description: The Clean Water Team research efforts during FY01 fall into three areas: watershed characterization, pollution prevention, and water treatment. The following provides a description of each.

Watershed characterization: The location and subsequent characterization of all the pollution discharge points on a watershed basis can be extremely difficult due to the aerial extent, rugged topography, limited land access, and disseminated discharges. NETL's characterization work offers a more efficient approach for accurately locating and mapping pollution sources through combined applications of airborne, geographical information system (GIS), and global positioning system (GPS) technologies.

NETL has pioneered the application of remote or airborne sensing technologies as new tools for the holistic assessment of watersheds. Remote sensing and geophysical technologies have been developed over the past half century for various applications, including national defense and industrial exploration (coal, gas, oil). The technologies being applied and evaluated by NETL (thermal infrared imagery, very low frequency electromagnetic field interactions (hereinafter termed VLF), magnetometry, and conductivity) are established and proven technologies. However, the application of this package of airborne technologies to watershed management is new. When various overlays (topographical maps, aerial photos, maps of underground mine workings, and geological maps) are combined with remote-sensing data, a holistic view of a watershed can be realized, as well as new perspectives for remedial approaches.

Watershed stewards, such as government agencies, industry, or watershed coalitions, armed with such a holistic view, can now make informed decisions, establish priorities, and provide specific direction to field people. Thus, field characterization is more efficient in terms of time and cost because of the increased accuracy of mapped pollution targets. Moreover, a preliminary assessment of a watershed can be completed prior to fieldwork to establish the presence or absence of potential water pollution sources (e.g., coal mines, sewage). This will make it easier to accurately identify and characterize the most common pollution types and will permit the strategic implementation of remedial measures that will maximize cleanup with a minimum expenditure of funds.

During FY99 and FY00, NETL collaborated with the USGS in conducting a low flow water quality synoptic survey and collected airborne thermal infrared imagery (TIR) in the lower Youghiogheny River basin between Connellsville and McKeesport, PA. During FY01, NETL compiled a comprehensive GIS database of this segment of river, which includes TIR, water quality, topographic, geologic, mine map, overburden thickness, coal structure, and other data. During FY01, NETL and the USGS received a PA Growing Greener Grant through the Penns Corner Conservation group to conduct an airborne geophysical survey of this same portion of the river.

The development of continuous and *in situ* monitoring technologies remains high on the list of priorities for government agencies responsible for environmental monitoring, exposure assessment, and environmental restoration. Superfund alone requires the identification, characterization, and cleanup of over 1600 to 2000 sites placed on the National Priorities List (NPL), and the typical annual costs for analytical services are on the order of $100 million. The U.S. Department of Defense currently spends more than $500 million per year to monitor contaminated surface, subsurface, and marine environments. To characterize each remediation site costs $0.6 to $1.2 million per site, and each soil or water sample costs about $100 to $1000 to collect and analyze.

The main limitation in the development and extension of miniaturized electronic sensors to the determination of compounds in untreated matrices has been the acquisition of molecular sensitivity. Biosensors, because of their specificity, fast response times, low costs, portability, ease of use, and continuous real-time signal, can present distinct advantages in specific cases (Rogers and Williams, 1995; Marco and Barcelo, 1996). Their biological base makes them ideal for toxicological measurements that are suited for health and safety applications. Biological components, such as enzymes and bacterial cells immobilized onto the surface of electrodes, can provide the necessary selectivity and allow the analyses of compounds that are not normally active at conventional electrode surfaces. Prototype biosensors reported for environmental applications measure a fairly broad range of compound classes, including phenolics, ammonia, formaldehyde, polycyclic aromatic hydrocarbons, nitrates, and metals, as well as a number of herbicides and insecticides (Ramanathan et al., 1997; Palmer et al., 1998; Barkay et al., 1998).

At hazardous waste sites, three major steps follow the preliminary screening and ranking of a site: characterization, remediation, and post-closure. Biosensors are particularly useful in the frequent and repetitive analyses at specific locations for particular compounds of interest. For example, real-time monitoring may be required to prevent off-site contamination of ground water, especially where flow patterns are quickly and dramatically altered as a result of remediation procedures such as soil excavation treatment and backfilling (Rogers, 1995).

Pollution Prevention: Fracture systems within stream channels can be created or enhanced by mining-induced subsidence. These fractures can divert a significant portion of the stream flow into underground voids, where it becomes polluted and discharged at some point down-gradient. Consequently, streambed fractures can cause both ground and surface water pollution and supply problems. NETL researchers have successfully used geophysical techniques (electromagnetic (EM) conductivity and VLF) within the stream channels to locate water loss zones by demarcating areas of high ground conductivity directly beneath the stream channel (Ackman et al., 1989, 1989, 1991). Cultural interference (e.g., buried metal objects, pipe lines, power lines, etc.) and near-surface layers of conductive clay and shale can cause false positives for these geophysical techniques. Therefore, stream gauging locations above and below the identified geophysical anomalies are needed to confirm and quantify water loss. Once the water loss zones have been located (generally to within a 10 meter accuracy) and quantified, shallow subsurface grouting activities can commence. A grid of shallow (1-m) injection holes can be drilled into the identified segment of damaged stream channel. In previous work, an expandable, two-component polyurethane grout was injected under high pressure into the broken rock strata beneath the stream channel. The grout quickly (within 30 seconds) hardened and contained the water in the stream channel. This approach negates the need to seal streams and stream segments that are not broken, which is conventionally done with some sort of lining technology. It is by targeting and sealing only the broken stream segments and not sealing unbroken segments that significant cost savings can be realized. Finally, unlike synthetic liners, no costly, long-term maintenance is required, and the aesthetics of the stream settings remain unaltered after sealing work is completed.

Watershed remediation and water treatment: The oil fields of the Appalachian Basin have problems that affect the economic and environmental health of the Nation, and these problems fall within the research mandate of the U.S. Department of Energy. Within PA, over one billion barrels of oil were produced prior to 1986, with an estimated 200 million barrels remaining in recoverable reserves (Penn-Brad Museum, 1990; Ross, 1996). Greater than 1 million barrels are currently produced annually. A major area of concern in the Pennsylvania oil fields is contamination of soil and water with crude oil. Numerous agencies and groups are concerned with the clean up of oil-contaminated soils, principally around plugged wells. The recovery of many older well sites to apparently pristine conditions provides circumstantial evidence that most oil pollution of the soil is remediated naturally, most likely due in part to the activity and adaptation of indigenous microbes and their use of the introduced hydrocarbons. Many examples exist in the literature that document the microbially-enhanced bioremediation of oil-contaminated sites on marine beaches (Button et al., 1992; Michel and Hayes, 1999; MacNaughton et al., 1999) and various soil types (Duncan et al., 1997; Balba et al., 1998; Foght et al., 1998). A principal goal of the current investigation is to determine the role of indigenous organisms in the degradation of crude oil in these regional soils. By determining the significance of the microbial participation in this process and examining whether this activity can be accelerated by the addition of nutrients, reasonable estimates concerning the probable time required for the "natural attenuation" of a site can be derived. This will provide regulators and independent producers alike with the scientific information needed to plan the reclamation and maintenance of oil production sites without undue economic hardship.

Because cleanup of the NPL sites is likely to take many years to accomplish, the EPA has been supporting research on temporary stabilization methods for contaminated soils and sediments (Diels, 1998; Schulz, 1989). Many of the sites are contaminated with metals, including zinc, lead, nickel, iron, copper, and mercury. These metals are capable of being immobilized in the soil if they are precipitated as metal sulfides. The sulfides, under the right environmental conditions, are more stable and less likely to be leached from the soils than other metal compounds. Naturally-occurring sulfate-reducing bacteria are capable of precipitating heavy metals as sulfides *in-situ* (Widdel, 1988). However, at these contaminated sites, the nutrients necessary for the bacteria to conduct metabolism are usually present in low concentrations, and their supply is dependent on the degradative activity of other organisms. The direct addition of specific carbon compounds and other micronutrients used directly by sulfate-reducing bacteria can allow this bacterial metabolism to occur (Hansen, 1993). The premise of the present research is that specific biopolymers (Klemchuk, 1990; Kulkarni et al., 1971; Middleberg, 1996) can be used in the field to drive bacterial sulfate reduction as the polymers naturally degrade to compounds used by the sulfate-reducing organisms.

Mine drainage from abandoned mined lands (AML) is a widespread problem in the Appalachian coalfields. Active treatment methods can be very expensive. For many mining companies, state and federal regulatory agencies, and public and private reclamation (watershed) groups, the only hope for affordable mine water treatment lies in some type of passive or semi-passive technology. NETL research personnel helped to develop many of the passive technologies. The four types of passive unit operations that are most commonly used to treat mine drainage are aerobic wetlands, compost wetlands, anoxic limestone drains, and down-flow reducing and alkalinity producing systems (RAPS), also referred to as vertical-flow wetlands (VFW) or successive alkalinity-producing systems (SPAS) (Hedin et al., 1994a). Aerobic wetlands promote oxidation and hydrolysis reactions and are effective when the raw mine water is net alkaline. Many of the discharges from large underground mine pools are net alkaline (Weaver, 1998). Compost wetlands and RAPS promote anaerobic bacterial activity, which can result in the reduction of ferric iron to ferrous iron, precipitation of metals as sulfides, and the generation of bicarbonate alkalinity (Kepler and McCleary, 1994). Anoxic limestone drains generate bicarbonate alkalinity and can be used to make mine water net alkaline and thus appropriate for subsequent treatment with aerobic wetlands (Turner and McCoy, 1990; Hedin and Watzlaf, 1994; Hedin et al., 1994b; Watzlaf et al., 2000). Limestone has been the alkaline material of choice for passive treatment because it is relatively inexpensive ($10-15/ton, delivered), its buffering capacity precludes overtreatment (pH is limited to about 8), and the iron sludge that forms is more dense than that produced by other alkaline chemicals.

Even the oldest wetlands and ALDs are only approaching 1/3 of their design life, and long-term data on the performance of these systems is needed. Systems to treat mine water containing aluminum have only been in existence for the past few years. Little is known about the longevity of these systems. These systems are typically constructed to facilitate flushing of aluminum and iron precipitates; however, data concerning the effectiveness of flushing is nonexistent. The limitations of each of these unit operations need to be understood so that passive treatment systems can be designed and constructed in an appropriate manner, given the chemical characteristics of the mine drainage to be treated. This team has maintained a long-term monitoring database of passive systems over the past ten years. The majority of passive systems being constructed world-wide are based on the selection and sizing criteria that were developed by NETL using empirical data from long-term monitoring. No other group has undertaken the rigorous, long-term monitoring program at a variety of sites that NETL has diligently maintained.

While many passive treatment systems have been very effective, there are many examples of failures, which unfortunately have generally not been documented. Many failures have occurred in the treatment of mine drainage that contain significant levels of aluminum (>10 mg/l). Acid mine drainage (AMD) containing aluminum can be quite detrimental to aquatic life. ALDs and several RAPS, which are typically used to treat this type of water, have experienced severe problems with clogging (Robbins et al., 1996; Watzlaf et al., 2000). It has not been determined to what extent the reduction in permeability in these systems is due to aluminum, iron, or other particulate precipitates. Successful long-term passive treatment of aluminum-containing mine drainage has not been documented. Most newly constructed RAPS are incorporating elaborate flushing systems to remove precipitated solids and maintain the necessary permeability to maintain flow rates through the system with the existing head pressures available. These systems are being periodically flushed. The effects of flushing, however, have not been quantified or documented. In addition, no quantitative data has been collected to develop guidelines for design of flushing systems or the duration, intensity, and frequency of flushing and their effect on permeability and subsequent effectiveness and longevity treatment.

Another important problem facing passive treatment systems is the relatively slow iron oxidation rates in aerobic wetlands. Many of the large volume underground mine discharges are net alkaline and only require aerobic wetlands for the oxidation, precipitation, and settling of iron. These discharges are typically 500 to 5000 gallons per minute and contain 40-100 mg/l of iron (>99% in the reduced ferrous state). Using current technology, large areas (up to 30 acres) would be required to treat these discharges. Iron oxidation rates are dependent on the concentration of dissolved oxygen and iron and the pH (which is strongly affected by dissolved carbon dioxide concentrations in the bicarbonate buffered water from passive treatment systems). The individual and combined effects of these parameters on iron oxidation rate need to be determined to develop more efficient and effective wetlands. In addition, the effects of wetland design (i.e., percentage deep and shallow areas and their ordering in the system, various passive aeration techniques (waterfalls, shallow ditches, etc.)) on these parameters need to be determined.

One problem facing passive treatment systems is the accumulation of iron-rich solids that reduce their ability to treat contaminated water. Currently, over 200,000,000 pounds of iron are discharged from coalmines in the United States each year (Hedin, 1996). Many passive systems are constructed to hold 10-30 years of precipitated sludge, but the sludge must eventually be removed to maintain treatment effectiveness, resulting in removal and disposal costs. AMD sludge may contain up to 70% (dry weight) iron and represent a potential economic resource. The iron oxide market in the U.S. is about 350,000,000 pounds per year, some of which is imported (Hedin, 1996). Iron oxides are commonly used as pigments, colorants, catalysts, and as additives to feeds and fertilizers. Limits are imposed on certain trace metals, depending on the application (Code of Federal Regulations, 2000). An integrated approach to characterizing mine drainage precipitates and determining the relationship between the precipitates and the associated water chemistry is necessary. Additionally, if it can be determined that iron oxides precipitated in passive treatment systems have chemical and physical properties comparable to those used by industry, they could be recovered and sold to offset treatment costs.

NETL has recently assessed the water treatment needs and options associated with the polluted underground mine drainage in the Swatara Creek watershed in eastern PA. The primary focus of these efforts has been the Rowe Tunnel mine site. Limited testing of treatment devices developed by NETL was also performed at the Tracy Air Hole and Indian Head Mine sites. Field evaluations have included new applications of NETL water treatment technology and the testing and development of new water-powered, water treatment technology. The ultimate goal is to provide a semi-passive treatment system, which makes use of local resources present at the site with a minimum of external inputs, other than periodic maintenance. The care of the site will be relinquished to the Swatara Creek Watershed Association for long-term operation. Thus, it will be necessary to keep operating costs and technical requirements to a minimum.

Research Objectives:

Specific research objectives for FY 2001 were to:

- Validate and evaluate subsurface remote sensing geophysical data acquired in FY 2000 using ground-based geophysical surveys, existing boreholes, and some drilling. Make remote sensing data accessible to the public.

- Demonstrate that groundwater flow paths can be mapped using geophysical data within approximately 300 feet of the surface with reasonable accuracy.
- Continue biosensor development and assess the response of probes to specific contaminants of concern.
- Continue to support volunteer watershed organizations on both a regional and national basis.
- Working in cooperation with other government agencies and local watershed organizations, develop and maintain a standardized training program for regional and national watershed organizations.
- Determine if passive systems constructed for the treatment of mine drainage can be reduced in size by incorporating alternative treatment processes. Assess effectiveness of passive systems intended to address problems such as oil well brines and high aluminum concentrations in mine drainage and investigate potential methods to improve their effectiveness.
- Develop a guidance manual on construction of passive treatment systems, updating our 1994 publication to incorporate new technology and new data.
- Assuming laboratory data continue to validate the technique, initiate field tests of NETL-developed technology for the *in situ* stabilization of metal-contaminated soils. Assess whether indigenous bacteria can be stimulated to accelerate remediation of oil-contaminated soils.
- Provide information that will aid industry in complying with Total Maximum Daily Loads.

LONG TERM GOALS / RELATIONSHIP TO NETL PRODUCT LINE(S): Thc Clean Water Team receives most of its funding from outside NETL. Funding sources during FY 2001 included EPA Region 3, EPA's National Lab in Cincinnati, the U.S. Army Corps of Engineers, and the States of Maryland and Pennsylvania. The biosensor work was funded by NETL's advanced research product line. The team's long-term goal is to establish a base of core funding within DOE though closer alliance with more traditional fossil energy product lines. Progress is being made, and it is hoped that this will be initiated in FY 2002.

Summary of Accomplishments:

Characterization

Airborne Thermal Infrared Imagery and Geophysical Investigations of the North Fork of Yellow Creek, Saline County, Ohio

High-resolution thermal infrared imagery was acquired from an airborne platform over 27 km^2 in the vicinity of Yellow Creek in Jefferson County, Ohio. The work was funded by the USACE. The imagery was georeferenced, projected, and warped using ground control points to within +/- 10 m (rms) with respect to map coordinates. Vector layers representing thermal anomalies where ground water meets the surface were extracted from the datasets using an apparent temperature thresholding technique. Numerous thermal anomalies could be extracted from the imagery. The database derived from these data will be used to target potential water pollution sources for field reconnaissance. Results obtained from the infrared imagery were used to successfully identify known ground water sources related to underground coal mining at the Hammondsville Remediation site on North Fork.

A hydrologic event breached the surface in an undermined section of streambed, diverting a portion of the mine drainage into the North Fork of Yellow Creek. A concrete plug was constructed by USACE to stop this flow. Concern was that the plug had been leaking. Through examination of the imagery, NETL investigators observed no significantly contrasting thermal signature near the concrete plug in North Fork. Had there been a significant flow from this area, it should have been readily apparent in the imagery.

Geophysical surveys were conducted along a 1-km length of the North Fork of Yellow Creek and across an adjacent AMD-impacted wetland. These surveys were carried out using an EM31 and an EM34-3XL, instruments that measure the apparent electrical conductivity of the ground. The EM31 measures ground conductivity to depths of about 20 feet, whereas the EM34-3XL with 10-m intercoil spacing has an exploration depth of about 45 feet. The objective of these surveys was to detect steeply dipping bedrock fractures that may permit groundwater flow between the stream/wetland and a coalbed that underlies the area at a depth of about 20 ft. A preliminary examination of the data has identified a large area of anomalous ground conductivity that contains two known sources of AMD.

Thermal Infrared Imagery and Geophysical Investigations of the Sulfur Bank Mercury Mine Superfund Site, Lake County, California

Nighttime thermal infrared imagery data were acquired over the Sulfur Bank Mercury Mine (SBMM) EPA Superfund site. Airborne Thermal Infrared was selected as a screening tool to assist in delineating potential areas of ground water evolution onto or near the surface since the Sulfur Bank area is geothermally active. The imagery was georeferenced, projected, and warped using ground control points. The thermal imagery was processed to enhance thermally contrasting areas employing color enhancement, density slice, and thresholding. Finally, the flight line image tiles were assembled into a histogram-matched and color-enhanced mosaic. Results indicate subtle thermally contrasting zones within the Herman impoundment that are in close proximity to known geothermal areas in the northern portion of the impoundment. There may also be indications of thermal anomalies immediately off shore, west of the rock dam separating Herman impoundment from Clearlake.

Daytime 6-band multi-spectral scanner (MSS) imagery was also acquired over the Sulfur Bank area. In addition to providing a geographically correct aerial image of the site for use as a mapping underlay, MSS can provide important spectral information on surface features. The reflected radiation from surface features are characteristic of the material from which they are comprised. These signatures were used to characterize all exposed surface features in the SBMM area through multi-spectral classification. The comparison of classification results over time can provide information on the effects induced by environmental changes. Examples found in the literature include the effects induced by climate and pollution on the types, distribution, and health of vegetation, fire potential, evaluation of revegetation success, detection of invading species, and eutrophication of water bodies.

Airborne and ground-based surveys were conducted at the SBMM Superfund Site to determine the likely pathways taken by contaminated groundwater leaving the mine. Airborne electromagnetic conductivity and magnetic data were used to delimit faults that could act as possible groundwater conduits. Airborne electromagnetic conductivity data also clearly showed the outline of a contaminated groundwater plume that extended from the flooded mine pit through a dam made of waste rock and into Clearlake, the largest freshwater lake in California. Previous attempts by EPA to locate this suspected plume using conventional drilling had failed.

Ground Geophysical Investigations at the T&T Mine Site, Preston County, WV

The objectives of this study were to determine the lateral extent of a contaminated mine pool located at a depth of about 300 feet and to determine areas of groundwater recharge to the mine pool. Down-hole geophysical logs were acquired from areas of anomalous conductivity identified by airborne surveys. The logs identified conductive lithologies and aquifers in the strata overlying the mine. These data were then compared with conductivity-depth models (modified Sengpiel) computed from multiple-frequency airborne-conductivity measurements to assess the accuracy and spatial correctness of airborne data.

Time-domain electromagnetic (TDEM) conductivity "soundings" were acquired at the locations of down-hole geophysical logs. TDEM sounding results were then compared with down-hole conductivity logs to determine if TDEM sounding could be used as a low-cost replacement for drilling and down-hole logging.

Ground Geophysical Investigations at the Miller and Peerless Mines, Montana

Electromagnetic (EM) conductivity, VLF, and vertical-gradient magnetometry surveys were conducted on pre-established grids at the Miller Mine and Peerless Mines in west central Montana. The Miller Mine survey was undertaken to determine the effect that grouting had on the distribution of groundwater within the overburden. No significant changes were noted from pre-grouting surveys. However, the area of grouting was well below the exploration depth for the techniques employed. Therefore, the grouting may have significantly affected the distribution of groundwater without being detected in these surveys.

EM conductivity, VLF, and vertical-gradient magnetometry surveys were also conducted at the Peerless Mine to replace erratic data from previous surveys at this site. A resistivity survey was also conducted to determine the groundwater flowpath through mine dumps.

Geographic Information System / Remote Sensing Laboratory

The Clean Water Team moved to new office space designed around a central work area, which functions as part of the GIS lab. This area contains state of the art hardware and software for the processing and interpretation of GIS and remote sensing data. The central work area also serves as a demonstration area for data display. The lab now contains 5 high-speed computer workstations, which are networked together through a local area network. This facilitates the sharing of data and allows for reduced software costs through networked licenses. In addition to upgrading computer hardware during the last year, the lab has expanded its data processing capability by adding remote sensing software (ENVI) and also upgrading to new GIS software, Arcgis® Version 8.1. Members of the Clean Water team received training in Arcgis® during the summer. In addition, two members of the team received advanced training in Arcgis® software at the 2001 ESRI (Arcgis®) Conference. The GIS lab also developed new methods for field mapping and data collection using a Palm Pilot® integrated with GPS. The lab purchased mapping software (ARCPAD® Version 5.0) that provides for a portable GIS system for field mapping and navigation to remote sites. Navigation to remote sites has been a critical element in the process of verifying remote sensing data.

Handheld computer running ARCPAD® software integrated with a GPS receiver.

This system was used to navigate to this remote mine discharge site along Sewickley Creek. Field data collected at the site was stored on the computer and later transferred to workstations in the GIS lab.

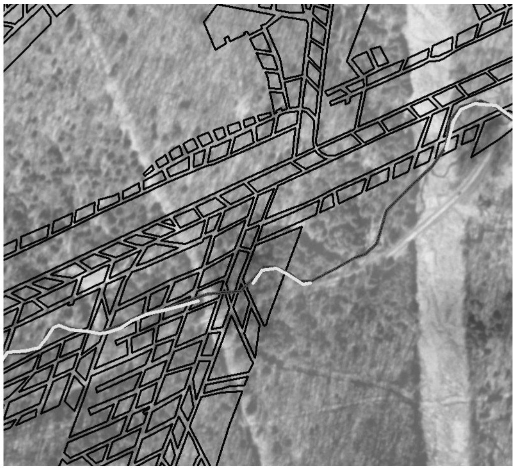
The GIS database of the lab continues to expand with each new project. The GIS database has been organized by project using a common projection (UTM) and datum (NAD83).

The GIS and remote sensing database has been a valuable resource to local university research projects. For example, West Virginia University is in the process of using NETL's airborne thermal data of the Monongahela River to evaluate hydrologic effects related to flooded underground mine pools on the Pittsburgh Coal seam. Federal agencies such as EPA, USGS, and OSM are also conducting research on the Monongahela River related to flooded underground mine workings and may also benefit from this data.

Kempton Mine Complex

The GIS database has been completed for the Kempton Mine complex. The database represents a very comprehensive environmental database in GIS format for the 35 square mile project area. More than 50 data layers have been developed for the project. All data layers are in the UTM 17 coordinate system with a datum set to NAD83. The Kempton GIS database contains detailed information on mine workings on the Upper Freeport coal seam. A digital elevation model (DEM) has been developed for the Upper Freeport coal seam based on structure contours digitized from paper maps. The Maryland Bureau of Mines completed the digitizing. In addition, an overburden thickness map has been developed from the coal elevation model and surface elevation grid. This dataset was developed using Arcgis® software and has been used extensively for analyzing the airborne geophysics data to locate potential losing zones in undermined streams. The results from this analysis were presented at the 2001 ESRI GIS users conference. The poster is being considered for publication in the Annual ESRI map book.

In addition, work at the Kempton Mine site has included collection and preliminary evaluation of airborne geophysical data, including multifrequency EM conductivity and total field magnetics for a 35 square mile area. At the present, airborne EM data show the most promise for application in focusing



Airborne geophysics data draped over USGS DOQ.
Mine workings on the Upper Freeport coal seam are shown in black. Measured water loss zones shown in yellow along Kempton Creek, shown as blue line. Red area from the airborne conductivity coincides with water loss zones.

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ground-based geophysical and intrusive investigations of undermined stream segments. By coupling airborne EM data with stream flow data and ground based EM-31 data collected by NETL Clean Water Team members, as well as overburden thickness calculated from existing data of coal structure contour elevation and surface elevation (mentioned above), a more sophisticated evaluation of airborne data can take place.

Development of Biosensors: Experiments using submitochondrial particles (SMP) as indicators of sediment pore water toxicity were carried out. Surface waters were collected for testing from the Monongahela and Youghiogheny Rivers. The SMP sensor approach exploits the shift in absorbance that takes place at 340-nm as fragments of mitochondrial membranes oxidize added NADH to NAD^+. Because the mitochondrial fragments are derived from beef heart muscle, the toxicity response of this system more accurately reflects toxicity to eucaryotic cells than do microbial systems, such as the Microtox system. In addition, the use of SMP in the sensor approach eliminates concerns over changes in the viability of immobilized whole cells.

A paper was presented at the Annual Meeting of the Society of Environmental Toxicology and Chemistry demonstrating the ability of gel probes to accumulate toxic compounds (e.g., Cu) that diffused laterally from the adjacent sediment pore waters. These compounds could then be extracted by diffusion into deionized water and subsequently tested for toxicity using the SMP electron transfer protocol. The paper identified the time required for probe equilibration *in situ* (ca. 3 hr) and extraction in deionized water (ca. 1 hr). Good correlation with initial copper concentration and toxicity was seen between 10 ppm and 100 ppm. Larger gels, or an alternative concentration approach, are necessary to determine toxicity at lower concentrations. One result of this presentation was a subsequent meeting with a commercial producer of SMP (MitoScan Corporation), who agreed to provide NETL with sufficient material to test the proposed probe concept in greater detail. The company also expressed an interest in establishing a formal research agreement with NETL.

The immobilized SMP probe concept was examined in greater detail. The original plan was to immobilize SMP in low-temperature gelling hydrogel, insert the probe into metal-contaminated water, and analyze the rate of NADH oxidation using a spectrophotometer or measure the loss of light intensity from NADH fluorescence under UV light. These initial studies were not successful due to the formation of metal precipitate in solution during probe incubation. The problem with this approach appeared to be the diffusion of alkaline buffer from the gel pore space into the metal (Cu) solution, causing the precipitation of an insoluble Cu hydroxide. A second approach was tested where gel without immobilized particles was first incubated in the presence of a Cu-containing solution. After a short period of incubation, Cu-containing gel was placed upon a “bed” of agarose gel containing the immobilized SMP. After a second period of incubation to allow Cu to diffuse from the gel into the SMP bed, the bed was flushed with an NADH solution, which fluoresces as a bright blue-white color under 302-nm UV light. Expected patterns of brighter light where NADH oxidation was inhibited due to higher Cu concentrations were not seen, although the detection system appears feasible. Additional experiments delineating the required times of gel incubation and metal transfer are planned.

Potential bacterial migration into gel probe agarose matrices: Experiments were carried out to investigate the extent of microbial migration into the gel matrix of environmental gel probe sensors. The agarose matrix of gel probes has previously been presumed to exclude microbes from the internal pore space, such that reactions occurring there are due to the molecular diffusion of various reactants. In addition, agarose gels immobilizing whole bacteria have been presumed to retain added bacteria due to the small pore size found in 2% agarose. Tests were done placing agarose gel probes in solutions containing either 1-μm diameter fluorescent beads or *Pseudomonas aeruginosa* grown in nutrient broth. After 3 weeks of incubation, neither gel beads nor bacteria had penetrated the agarose matrix, as determined by direct fluorescence microscopy. These tests indicate that bacteria were effectively excluded from the environmental probe matrix.

Submicron silver detection of mercury: Experiments were carried out using submicron silver particles as adsorbents for mercury in aqueous solution. These experiments established the time course of mercury removal and the association of mercury with the silver particles. Submicron silver particles removed >99% of an initial concentration of 750 μg/l (ppb) mercury after 5 minutes of incubation. The ability of silver particles immobilized in a hydrogel matrix to remove mercury from solution is currently under investigation. Ultimately, silver particles will be placed in sediment gel probes for the *in situ* detection of mercury in contaminated sediment pore waters.

Fluorescence response of metal-sensitive dyes: Experiments were carried out to examine the fluorescence response of the dye Newport Green applied to various heavy metals that diffused into an agarose matrix. This dye fluoresces brightly under UV light in the presence of specific metal ions, such as cadmium, zinc, copper, and nickel. A multi-well diffusion approach was used to test the relative fluorescence response to each metal, and these tests suggested that the strongest response of the dye was to nickel, followed by zinc. Agarose gels (1%) were made up as sediment gel probes and were incubated in 25-μ<u>M</u> metal solutions of Cd, Zn, Cu, and Ni. Probes incubated for 10 minutes were flushed with a solution of 10 μ<u>M</u> Newport Green and exposed to UV light in the chemiluminescence dark box. Integrated digital photos of the resulting images showed that the dye was extremely sensitive to the presence of nickel and fluoresced brightly, with other metals also eliciting a fluorescence response, but much less bright. *Pseudomonas aeruginosa* strain RM 4-440 was rejuvenated on LB medium for renewed investigation of its capabilities as an immobilized luminescent reporter of selected toxic compounds in soils and sediments. A field fluorometer, purchased for the determination of total petroleum hydrocarbons in contaminated soils, is being adapted to investigate novel detection methods in bioprobes using the specific fluorescence of unique dyes. These applications include the quantification of protein levels (NanoOrange) and the viability of bacteria (LIVE/DEAD BacLight assay and YOYO-1).

Passive Remediation of Contaminated Soils and Sediments using Biodegradable Polymers

Various degradable polymers were added to the sediments of a wetland receiving AMD in Jefferson County, PA. Several of the polymers tested were unacceptable for environmental application because they degraded too rapidly, did not degrade rapidly enough, or were too difficult to place in the environment. For example, biodegradable plastic bags containing polycaprolactone and starch degraded rapidly, but also tended to float in the acidic water of the wetland. Abiotic hydrolysis of various polylactic acid (PLA) polymers demonstrated differential rates of lactate production based on polymer molecular weight and particle size. Acid volatile sulfide concentration and pH, indicators of increased indigenous bacterial sulfate reduction activity, increased in sediments receiving polymers that generated soluble lactate. Limestone additions to lab experiments were beneficial to polymer degradation and bacterial activity, but the pH at the field site was apparently too low to allow the amount of added limestone to have a positive effect. It was concluded that polymers added at field sites would have to be mixed below the sediment-water interface (rather than being deposited on the surface) to significantly enhance bacterial activity.

A second field experiment was established in the same AMD treatment pond in Jefferson County, PA in May 2001. Ten buckets received wetland sediment and biodegradable polymer-amended compost prior to being placed in the pond. PLA polymers 1, 2, and 3, corresponding to low molecular weight/low residual lactide, high molecular weight/low residual lactide, and high molecular weight/high residual lactide, respectively, were tested along with polyglycolic acid and controls. It is expected that the polymer amendments will differentially influence the activity of sulfate-reducing bacteria, and the production of alkalinity and acid-volatile sulfides over time. A rapid method for the determination of sulfate-reducing bacteria in these experimental buckets using a microplate/MPN method was tested and compared favorably with more time-consuming alternative approaches. The field site will be sampled in May 2002.

Scanning electron microscopy images of polylactic acid beads incubated in an acid mine drainage wetland sediment for 4 months were analyzed. These images revealed smooth surfaces inconsistent with microbial attack. The appearance of the beads suggests that only abiotic hydrolysis of the beads occurs, and that the pH in the immediate vicinity of the beads may be too low to allow bacterial attachment, although released monomers may be used after they diffuse through porewaters and become less acidic via neutralization.

Polylactic acid beads were added to unmixed Bradford, PA soils that received crude oil and fertilizer amendments. Because some aromatic hydrocarbons are selectively degraded by sulfate-reducing bacteria, an experiment was designed to see if the slow release of lactic acid might stimulate hydrocarbon degradation. No decrease in total bacterial populations was seen in the polylactic acid amended soils relative to other controls. Influence on total petroleum hydrocarbon component concentrations is currently being analyzed. The similar potential use of this method to inactivate nitroglycerine at historic waste sites in Pennsylvania via the stimulation of hydrogen sulfide is being discussed with the appropriate landowners.

An historic lead-contaminated site was visited and sampled in Venango County, PA. The Boughton Acid Works processed spent sulfuric acid from refineries in Titusville for over 50 years, eventually closing in 1917. Soil sampled at this site was extremely high in total lead (2,000 – 41,000 ppm), presumably due to the use of lead-lined acid boilers and holding tanks. This site may be representative of those that may benefit from degradable polymer treatment to further immobilize biologically available lead. Remediation of private and government firing ranges contaminated with lead shot may require similar treatment approaches to those that could be employed at this site. Laboratory studies investigating potential lead immobilization via the addition of polymer amendments are underway.

Agar plates containing emulsified polylactic acid (PLA) and polycaprolactone polymers were surface spread with dilutions of sediments from a mine drainage treatment system that had been incubated for over one year with various organic carbon amendments. Clear plaques that developed on these media were subsampled for the bacteria or fungi present. Isolated organisms were transferred and purified for further identification. Initial isolation of pure cultures suggests the presence of depolymerase enzymes in several different actinomycetes and bacteria.

Four different biodegradable polymers were placed in nylon mesh bags and were placed in different aqueous environments to assess their degradability in situ. Net weights of the polymers over time will be determined, as well as microbial populations colonizing the polymers. The mass of polyglycolic acid in nylon mesh bags decreased approximately 20% after two months *in situ* incubated in an acid mine water environment. These experiments will establish the natural degradation rates to be expected for these polymers in normal and low pH aqueous environments and indicate the types of microorganisms that can degrade them.

Soils from a zinc smelter in West Virginia that received polymer amendments continued to be monitored. Establishment of anaerobic conditions and the formation of metal sulfides has been extremely slow, presumably due to the extremely oxidized state of materials that passed through the smelter. Only those soils receiving one of 3 different polylactic acid amendments and gypsum had metal sulfide precipitates and low redox potential characteristic of bacterial sulfate reduction. Polymers or gypsum alone did not stimulate bacterial sulfate reduction activity.

Training Videos for Watershed Groups

NETL, in collaboration with its federal and state partners, has completed the production of the initial master video, which will serve as an introduction to subsequent training videos and as a basic educational and promotion product for volunteer organizations. The completed master (introduction) video was provided to all team participants and selected watershed organizations for review and comment.

Pollution Prevention

Nanticoke Creek Stream Sealing Study

Base-line data collected for the Nanticoke Creek site includes stream flow, geophysical and geographic data. The United States Geologic Survey (USGS) regularly collects stream flow data at several gauging stations across the area of interest on Nanticoke Creek. This data is collected so that areas of water loss can be identified along the stream length of interest. If stream flow at a gauging station downstream is significantly less than stream flow of an adjacent upstream gauging station, the stream length between the two gauging stations is targeted as an area of flow loss to the underlying mine through subsidence-related or natural fracture systems. It has also been used to determine the effectiveness of stream grouting efforts carried out at the study area by the Clean Water Team. NETL Clean Water Team and PA DEP personnel have collected various types of ground based geophysical data at the Nanticoke Creek site: shallow electromagnetics (EM), mid-depth EM, and VLF.

Using an EM-31 apparent conductivity instrument manufactured by Geonics, shallow EM data was collected along a 1000-foot stream segment. By collecting data in the streambed, areas of relatively high conductivity (water-filled fractures and subsidence related voids within the first 6 meters below surface (about 20 feet)) were detected. These EM-31 data were used to pinpoint grouting to areas as small as one square meter.

Mid-depth EM data were collected adjacent to Nanticoke Creek using the Geonics EM-34 instrument. Operating at a 20-meter transmitter/receiver coil separation, measurements represent apparent conductivity at a skin depth of approximately 30 meters (about 100 feet). These EM-34 data depicted areas of low conductivity, which when integrated into a GIS database, correlated extremely well with mapped water loss zones in the stream, mine openings and coal outcrops on the surface. The observed low conductivity values (dropouts) are related to air in the subsurface, which is significantly less conductive than soil, rock or water. These large air pockets (in the subsurface) correspond with observed surface openings that ventilate mine air to the atmosphere.

VLF data were collected using an ABEM WADI VLF receiver, which is also an electromagnetic instrument. Used primarily by the United States Navy for submarine communication, VLF signals are generated at 23 transmitting stations located around the world and propagate thousands of miles in all directions. However, from a non-military perspective, this technology has proven to be effective in locating geologic and hydrologic (vertical water-filled fractures) features (McNeill, J. and Labson, V., 1990). Using a hand held receiver, these signals are received from relatively close transmitting stations. Local conductive bodies in the subsurface generate a secondary electromagnetic field and these anomalies are received and recorded by the VLF receiver. Preliminary results suggest that an anomalous VLF response correlates very well with locations of known coal outcrops, areas of stream flow loss, and other geophysical anomalies.

Survey data was collected for the Nanticoke Creek study area in order to ensure spatial accuracy of collected data and observed relationships. In addition to a high accuracy land survey conducted by NETL employees, differential GPS data was collected to verify location of various points in X, Y and Z real world coordinate space. Finally, previously acquired data from an aerial survey provided two-foot contour data that was used to develop a high-resolution digital elevation model for three dimensional visualization and evaluation of data.

In order to investigate spatial relationships between data of various sources, data were collected and integrated in a geographic information system (GIS). Development of a GIS database allows incorporation of aerial photography, mine maps, high accuracy GPS survey data, high-resolution digital elevation model, stream flow, geophysical, and other data into a spatially related database. This allows for a spatially explicit evaluation of complicated systems and surface/subsurface interactions in three dimensions.

Previous investigations and experimentation by the NETL Clean Water Team have successfully employed a novel stream grouting technique to prevent flow loss from streams to underlying mines in areas of bituminous coal mining. The Nanticoke Creek study is the first attempt to apply this technique to remediate streams adversely impacted by anthracite coal mining and to test a new, single-component polyurethane grout. To date, two grouting sessions have been carried out at the Nanticoke Creek study area. Baseline flow and geophysical data were collected to establish existing conditions and pinpoint areas of interest for grouting. After stream grouting, flow measurements and geophysical data were collected along the stream to determine changes in subsurface hydrologic conditions resulting from grouting efforts. Based on evaluation of these new data, a second session of drilling and stream grouting was carried out to augment the first session. After this second grouting session, flow and geophysical data were again collected to determine the success of the grouting efforts. To date, grouting efforts at the Nanticoke Creek study area have met with little success. Effective site characterization and increased understanding of site hydrologic conditions and mining history have led to the development of a new strategy for stream grouting at the Nanticoke Creek study area.

Watershed Remediation and Water Treatment

Bioremediation of Oil Production Sites

Soils at bioremediation sites in Bradford, PA were sampled and analyzed for total petroleum hydrocarbons (TPH) by GC-MS. Data showed that alkanes were preferentially degraded or lost at the sites, especially at older bioremediation sites. The only site with TPH concentrations low enough to warrant closure had been flooded and presumably lost much of the hydrocarbon content by this mechanism. Large differences were seen in the relative abundance and ratios of various specific aromatic compounds and classes of aromatic compounds, suggesting different mechanisms for oil degradation at field sites. Distillation of one gallon of typical Bradford crude oil yielded 35% gasoline, 15.1% kerosene, 15.3% gas oil/heavy kerosene, 16.2% wax distillate, and 18.4% bottoms/residue, with an API specific gravity of 44.2.

Bench-scale experiments were carried out examining the bioremediation of crude oil in soil collected from a proposed bioremediation site in Bradford, PA. The influence of initial oil concentration and fertilizer amendment on the rate of hydrocarbon degradation was examined. In addition, two novel amendments (magnesium peroxide and polylactic acid, which supply oxygen and lactic acid, respectively, as they decompose) were tested for their influence on bioremediation. Experiments were carried out for 80 days and samples for total bacteria and TPH were taken every two weeks. Data demonstrated that the addition of crude oil alone resulted in a considerable increase in total heterotrophic bacteria, and that the addition of fertilizer resulted in a further significant increase in total bacteria. Sodium azide (used as an inhibitor of bacterial activity) reduced, but did not completely eliminate bacterial populations in control soils. Addition of 8% crude oil resulted in the same observed effects on bacterial populations as 4% crude oil. This is significant since the bioremediation sites at Bradford routinely receive far more oil initially than is recommended by standard practices. TPH samples were submitted for outside laboratory analysis by GC-MS. These data showed that the degradation of many classes of hydrocarbons (esp. alkanes, naphthalenes and fluorenes) was significantly enhanced in fertilizer-amended soils. Because of these studies, the EPA added recommended fertilizer amendments to their existing bioremediation sites.

A new bioremediation site (McCracken #2) was established in Bradford, PA in July 2001. This site received ca. 650 gallons of crude oil sludge and oily soils associated with the cleanup of abandoned well sites. Necessary fertilizer requirements for this site were calculated and applied by EPA. An areal map of initial TPH distribution within the bioremediation site was determined by analyzing for TPH using a field fluorometer. Soils were sampled at 20 locations within the site, and TPH extracted with methanol prior to analysis. Determined values corresponded well with independently determined GC-MS TPH analyses of sample splits and demonstrated the inherent heterogeneity of initial oil distribution at the bioremediation sites. In laboratory experiments, sodium azide was found to have a quenching effect on TPH fluorescence, making it a poor choice as a bacterial inhibitor when using this analytical approach. Some minor fluorescence was also observed for the fertilizer mix used in the laboratory experiments.

Samples collected from the McCracken #2 site and other bioremediation sites were submitted for molecular biological analysis of bacterial populations via denaturing gradient gel electrophoresis (DGGE) and the identification of phospholipid fatty acids (PLFA). These samples are currently being analyzed. Equipment was obtained to allow in-house DGGE analyses in the future.

A laboratory experiment was set up to examine the maximum load of crude oil sludge that Bradford soils could initially receive without having a detrimental effect on rates of bioremediation. Increasing amounts of the same sludge applied at the McCracken #2 were added to Bradford soils with hay and fertilizer amendments. This experiment was subsampled routinely for total bacterial numbers and TPH. Data showed a stimulatory effect on microbial population size up to 5% crude oil sludge addition, with a decrease at 10% addition. In addition, soil particle sizes increased with increasing oil sludge addition, presumably resulting in a smaller surface available for bacterial activity and hydrocarbon biodegradation.

Samples collected from older abandoned oil sites (tank and pump jack residues) showed that these materials were greatly enriched in aromatic hydrocarbons and heavy metals. Samples were typically enriched in As, Ba, Cd, Co, Cr, Cu, Ni, Pb, and Zn, relative to controls.

Passive Treatment

The reader of this report may not realize that the selection and sizing guidelines currently used to design mine water passive treatment systems in the United States and, in fact, the world, were developed by ES&T researchers. These guidelines were developed using long-term, comprehensive, data from numerous passive treatment systems, as well as results from laboratory- and pilot-scale tests. Due to our reputation in passive treatment research, we are often asked to lend technical assistance. We continue to advise the U.S. Army Corps of Engineers on passive treatment systems for the Powell River Feasibility Study. We have assisted the Peters Creek Watershed Association (PA) and Sewickley Creek Watershed Association (PA) in identifying and characterizing mine drainage discharges, setting up a monitoring program, developing passive treatment strategies, and acquiring funding for implementation of passive treatment in each watershed. We have provided technical assistance to the Maryland Dept of the Environment to design passive systems in the Elklick Run Watershed. We have also assisted the Monastery Run Wetland Group (PA), Elizabeth Mine Study Group (VT), Slippery Rock Watershed Coalition (PA), Mill Creek Watershed Coalition (PA), Clarion River Watershed Improvement Committee (PA), PA Dept of Environmental Protection, U.S.

Dept of Agriculture, U.S. Forest Service, and the Korean Coal Industry Promotion Board. Other countries that are beginning to implement passive treatment have also expressed interest. Recently, ES&T personnel have traveled to Spain, South Africa, and Brazil to present our research results.

Monitoring and Evaluation of Full-scale Passive Treatment Systems

In FY01, numerous passive treatment sites were monitored to assess the long-term performance of various types of unit operations used to passively treat mine drainage (Table W1). Each site has been monitored at least twice (winter and summer). Fifteen new sites have been identified, visited, and monitored. Four of these sites will be added to the existing long-term monitoring assessment program. Water quality databases have been updated. Data have been analyzed and the results have been presented via presentations and publications. One ALD (at REM) has failed after 9 years of effective treatment, apparently due to clogging with iron and/or aluminum precipitates. Plans are currently underway to upgrade the passive treatment system at this site. We will attempt to coordinate with these plans to autopsy the ALD to verify the cause of failure.

Table W1. Passive sites currently being monitored.

Site	**Unit Operation**	**Duration of Monitoring (years)**	**Location**	**Watershed**
Howe Bridge	ALD	10	Jefferson Co., PA	Mill Creek, Clarion River, Allegheny River
	ALD	7		
	RAPS	10		
	Ponds/wetlands	10		
Morrison I	ALD	11	Clarion Co., PA	Clarion River, Allegheny River
	Ponds/wetlands	11		
Morrison II	ALD	3	Clarion Co., PA	Clarion River, Allegheny River
	Ponds/wetlands	3		
Oven Run D	RAPS	6	Somerset Co., PA	Stony Creek River, Conemaugh River, Allegheny River
	RAPS	6		
	Ponds/wetlands	6		
Oven Run E	RAPS	4	Somerset Co., PA	Stony Creek River, Conemaugh River, Allegheny River
	RAPS	4		
REM	ALD	9	Jefferson Co., PA	Little Mill Creek, Mill Creek, Clarion River, Allegheny River
	ALD	9		
Filson	ALD	7	Jefferson Co., PA	Little Mill Creek, Mill Creek, Clarion River, Allegheny River
	ALD	7		
Jennings	RAPS	8	Butler Co., PA	Big Run, Slippery Rock Creek, Connoquenessing Creek, Beaver River, Ohio River
	Ponds/wetlands	8		
De Sale I	RAPS	New	Butler Co., PA	Seaton Creek, Slippery Rock Creek, Connoquenessing Creek, Beaver River, Ohio River
	RAPS	New		
	Ponds/wetlands	New		
	Limestone Bed	New		
De Sale II	RAPS	New	Butler Co., PA	Seaton Creek, Slippery Rock Creek, Connoquenessing Creek, Beaver River, Ohio River
	RAPS	New		

	Ponds/wetlands	New		
	Limestone Bed	New		
Scrubgrass	Aerator	New	Allegheny Co., PA	Scrubgrass Creek, Chartiers Creek, Ohio River
	Ponds/wetlands	New		
Elklick	ALD	7	Garrett Co., MD	Elklick Run, Potomac River - North Branch, Potomac River
	Ponds/wetlands	7		
Masteller	RAPS	3	Garrett Co., MD	Elklick Run, Potomac River - North Branch, Potomac River
	RAPS	New		
Schnepp	ALD	8	Jefferson Co., PA	Mill Creek, Clarion River, Allegheny River
	Ponds/wetlands	8		
Penn Allegh	Aerator	New	Allegheny Co., PA	Lardinton Run, Bull Creek, Allegheny River
	Ponds/wetlands	New		

Effectiveness of Aluminum Removal in Passive Systems

The amount of metals retained within the two parallel Desale II RAPS has been accurately quantified since their construction in the fall of 2000. One of the RAPS at the Desale II site was flushed this summer. This event was monitored very closely to enable the quantification of metals removed during this flushing event. Each of 8 discharge pipes were flushed for 9 minutes with samples collected every 15 seconds for the first minute, every 30 seconds from 1-5 minutes and every minute from 5-9 minutes. The flushed water was very turbid for the first 2-4 minutes for each flush pipe. Flow, an important measurement for load quantification, was determined using three methods: 1) timed volumetric measurements, 2) measurement of the horizontal distance the water fell four vertical inches, and 3) measurement of the elevation drop in the RAPS pond. Dissolved oxygen and pH were continuously monitored and recorded at each sampling interval. Preliminary analysis indicates that only a very small percentage of iron and aluminum precipitates was flushed during this event. Longer flushing times for each individual discharge pipe is recommended. The effectiveness of this type of flushing will be determined for the other RAPS at this site.

Characterization of Iron Hydroxide Precipitates in Mine Drainage Passive Treatment Systems

In a separate task, iron hydroxide precipitates have been characterized. Over 50 sludges and associated water samples originating from 3 different coal seams were collected from passively treated and untreated discharges located in Pennsylvania and Maryland. Major and trace elements were determined using an inductively coupled argon plasma atomic emission spectrometer (ICP-AES) following acid digestion and by instrumental neutron activation analysis (INAA). Mineralogy and morphology were determined using a Phillips X'PERT diffractometer and a scanning electron microscope, respectively. Iron content ranged from 25 to 68% (dry wt.) with goethite as the dominant mineral (40-90% (dry wt.)). Ranges of concentrations for other trace metals are included in Table W2. The majority of the particles were found to have a spiky spherical morphology with 0.5-2.0 micron diameters. Within several passive treatment systems, iron content remains relatively constant, and concentrations of Mn, Co, Ni, and Zn increase, while As concentration decreases. Our preliminary conclusions indicate that some sludges are suitable for industrial and manufacturing uses. Certain precipitates contain anomalously high concentrations of trace elements, which may prevent use as an additive to cosmetics or food (e.g., As). These associations could be related to the depositional environment of the coal seam from which the discharge originates. Subsurface cation exchange and sorption processes can influence the trace elements that accumulate in the sludge. Sequential extraction procedures will be carried out to help determine trace element associations and to assess how tightly trace elements are bound to the iron hydroxide precipitates.

Table W2. Elemental composition of various sludges

Element	Content (dry)
Fe	25 - 68 wt%
Mn	0.01 - 3.59 wt%
S, Al	<2 wt%
As	Up to 3000 ppm
Co	Up to 1060 ppm
Ni	Up to 700 ppm
Pb	13 - 41 ppm
Zn	Up to 760 ppm
Cd, Cu	<5 ppm

Development of Semi-Passive Technologies

Two approaches to the development of semi-passive technologies have been pursued this year. The first involved an attempt to model the rate of iron oxidation in small, laboratory-scale field tests and in existing passive and semi-passive systems. The objective is to develop a mathematical model that can be used to demonstrate the effect of system modifications on the extent of iron removal. The quantitative model then can be used to improve the construction criteria for future passive systems as well as to predict the effect of the addition of an active unit operation, such as aeration. In the second approach, we are participating in the design, construction, and operation of large-scale experimental semi-passive systems. These in-stream systems allow for the application of various active-treatment options at field locations. The design of these systems includes the ability to demonstrate the effectiveness of water-powered devices as a cost-lowering alternative to electric- or fossil-fuel-powered devices. These two approaches are considered complementary, one providing the science-based remedial approach, the second providing the on-ground demonstration of its effectiveness.

Iron Oxidation Rates

In the first approach, iron oxidation rates under different conditions were measured at three sites during FY2001. At the Morrison site, the iron oxidation rate was measured under totally passive conditions. The Scrubgrass Run site had active aeration of the mine drainage, but all subsequent unit operations were passive. At the Wilson Run site a laboratory-scale, field-deployable apparatus was used to investigate the effect of continuous, active aeration. Despite the different experimental conditions, the results at the three sites indicated that efficient gas exchange was the factor limiting the iron oxidation in these alkaline waters.

In the passive treatment system at the Morrison site, iron oxidation rates were modeled using pH, temperature, dissolved oxygen and iron concentrations. The system consists of a 224-m ditch receiving the effluent from an anoxic limestone drain (ALD), which treats drainage from a reclaimed surface coal mine in Clarion County, Pennsylvania. The ditch was divided into ten sections. Depth and width were measured for each section. Three water samples (raw, unfiltered and acidified, and filtered and acidified) were collected at the beginning and end of each section. Water analyses included field-measured pH, dissolved oxygen, temperature, and laboratory-measured net acidity and major and trace element concentrations (including Fe^{2+}, Fe_{TOT}, Ca, Al, Na, Mn, SO_4^{2-}, K, As, Ba, Be, Cd, Co, Cr, Cu, Ni, Pb, Sb, Se, and Zn). Field pH, dissolved oxygen, and temperature varied between 5.89-6.37, 0.52-7.75 mg/L, and 12.1-22.0 ^oC, respectively. The average flow rate for the system was 92.8 L/min. Iron concentration decreased to approximately 70% of the original level by the end of the ditch. A kinetic model for the loss of ferrous iron from solution was compared to the traditional sizing criteria for iron removal of 10-20 $gd^{-1}m^{-2}$. Because of the geometry of the ditch, a plug flow model was used. The majority of the sections had removal rates near the 20 $gd^{-1}m^{-2}$ traditional value, and modeling provided insight as to why certain sections performed better than others did. All significant changes occurred soon after aeration, indicating that net alkaline water should be aerated immediately in order to optimize iron removal. The kinetic parameters obtained at this site were used with the site-specific initial iron concentration, temperature, DO, and pH to predict the extent of iron removal at two other sites. At the Penn Allegheny site, the removal in a pond receiving mechanically aerated water with an influent iron of 58.6 mg/L was predicted to have an effluent concentration of 16.4 mg/L and was found to have an actual effluent concentration of 19.7 mg/L. Also, the removal in a pond at Elklick receiving naturally aerated ALD effluent with an influent iron concentration of 38.1 mg/L was predicted to have an effluent concentration of 0.1 mg/L and was found to have an actual effluent concentration of 0.2 mg/L. Thus, the model might be somewhat less site-specific than it was initially thought to be, but the data set is too small for any generalizations.

The mine drainage at the Scrubgrass Run site is anaerobic, net alkaline, and has a pH around 6. The drainage is directed by way of a short ditch to an electric-powered air-blower. The effect of the blower is to increase the DO to near saturation levels and to increase the pH by 0.5 units. The effectiveness of the aeration was determined by capturing samples of the water before and after the blower and following the ferrous iron loss with time. It was found that the aeration accelerated the iron oxidation initially so that the extent of iron loss over the first 20 hours for the aerated sample was 3 times that of the non-aerated sample. However, after about 24 hours, the rate for the non-aerated sample appeared to be equivalent to that of the aerated sample. Presumably, the natural gas exchange had eventually increased the DO and pH in the non-aerated sample to the same levels as in the aerated sample.

A laboratory-scale aeration apparatus was used at the Wilson Run site. In this case, a 1.5L sample of the net-alkaline mine water was actively aerated continuously. Although the DO increased to near saturation within 45 minutes, the rate of iron loss was negligible. Only after sufficient de-gassing of carbon dioxide occurred and the pH rose from an initial value of 5.6 to about 7 did the iron loss accelerate**.**

Experimental Semi-Passive Treatment Systems

In the second approach, the construction of an experimental semi-passive treatment system was undertaken this year, and planning for a second one has begun. The first system is on Lorberry Creek in the Swatara Creek Watershed. The high flow (2000 GPM), low iron concentrations (5-15 mg/L), and steep terrain at this site make it unsuitable for typical passive-treatment technologies. A second site being considered is in West Virginia; it has a steep terrain, high iron concentration, moderate flow, and a very limited amount of space, making it a poor candidate for a totally passive system.

At the Lorberry Creek site, completed tasks include site characterization and evaluation of metals removal options. A detailed water quality sampling of the mine drainage at the Rowe Tunnel and along Lorberry Creek have been completed through a collaborative effort with USGS. Because of this site characterization work, NETL has determined that water treatment (neutralization, oxidation, and/or solids removal) is necessary to remove the metals and reduce pollution loading in Swatara Creek. NETL designed an experimental "semi-passive" treatment system for Lorberry Creek during FY01, which will allow us to test simple, low-cost water treatment technologies. The design included the use of water-powered equipment for chemical addition and solids removal and an aerobic wetland for solids separation. The design accommodates the use of various treatment reagents, including alkaline waste materials (e.g., lime kiln dust), variations in system flowrates, and oxidation techniques (passive and mechanical).

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